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(54) Title: A COMPOSITION FOR USE IN THE TREATMENT OF A SURFACE

(57) Abstract: A composition for use in treating a surface, comprising a polyorganosiloxane having formula (A) : T. R^1 R^2 SiO(R^3 R^4 SiO)$_r$ (R^5 T. SiO)$_s$ SiR^2 R^3T, wherein the symbols R^1, R^2, R^3, R^4 and R^5, which are identical or different, represent a phenyl or a C_1 to C_6 alkyl radical, the symbols T, which are identical or different, represent a phenyl, a C_1 to C_6 alkyl radical, or a polyoxyalkylene ether residue of formula: --R--O--(R'O)$_n$ R" or a amino group of formula: --(NR'R"R"')$^+$ Z$^-$, wherein R' and R" are identical or different and represent a C_1 to C_{19} alkyl radical or C_3 to C_{15} alkylene group or branched $C_{4\text{-}15}$ alkylene group, the unit (R'O)$_n$ represents a poly(ethylenoxy) or poly(propylenoxy) group, n is an average value ranging from 5 to 200, and Z represents an acetate anion. r is an average value ranging from 1 to 10, and which interact with said biocidal agent. s is an average value ranging from 1 to 100; and an active agent.

A COMPOSITION FOR USE IN THE TREATMENT OF A SURFACE

The present invention relates to a composition for use in the treatment of a surface, and particularly to a polymer composition and a process for use in disinfecting a surface or the like.

In certain environments, it is often required to disinfect surfaces, implements or the like. In the food industry, for example in food preparation and processing plants and restaurants, considerable time and effort is spent in disinfecting areas and surfaces for preparation of food products to prevent cross contamination from such areas or surfaces into the food products. Likewise, in other industrial or medical environments, for example in hospitals, it is particularly important to disinfect working surfaces and instruments so that medical operations and patient care can be carried out in a sufficiently sterile environment. In commercial or domestic environments, for example in offices or kitchens, it is equally important to be able to clean and disinfect suitable surfaces. Many compositions or reagents are known which contain active ingredients for disinfecting surfaces. However, many of these compositions may be difficult to prepare or use due to toxicity considerations or difficulty of application. Further, and more particularly, after disinfection of the treated surfaces, the surfaces are susceptible to recontamination.

US-B-6,465,409 discloses an aqueous composition comprising a biocidal agent and a polyorganosiloxane containing water-soluble or water-dispersible polyether groups. The composition is used for disinfecting hard surfaces, such as floors, walls and work

surfaces. However, after the composition has been applied to a surface the biocidal agent can only be released in a controlled manner when the surface is treated with an aqueous medium, typically water. This is a major disadvantage because bacteria or other microorganisms present on the surface can only be killed when the biocidal agent is released from the composition on the surface and this only occurs when the surface is made wet. Consequently, bacteria and germs can accumulate on surfaces treated with the composition over time and after the surface has been washed. This means that if the surface has not been washed for some time and it is used, for example, to prepare a food product or to conduct a medical operation in which it is important to have a disinfected surface, a substantial amount of bacteria or germs may be present on the surface leading to cross contamination.

Furthermore, the amount of biocidal agent that may be released from the composition is limited to the volume of the aqueous medium in contact with it. If a sufficient amount of water is not used to clean a surface, an insufficient amount of biocidal agent may be released meaning that all of the micro organisms present on the surface may not be killed. A further disadvantage is that the entire surface must be cleaned with water in order to release the biocidal agent to disinfect the overall surface.

GB-A-2,338,651 discloses a liquid polymer composition comprising polydimethylsiloxane and its use in treating surfaces, such as glass. The composition may be applied to a surface, where it bonds to the surface and may kill micro organisms present on the surface when the composition is dry. However, this composition relies on acid-etching of the surface prior to bonding and therefore may

be difficult to apply and damaging, if contacted, by the user. Furthermore, the composition needs to be wet in order to be active.

There has now been developed an improved composition for use in disinfecting surfaces, implements or the like which has a substantially long lasting effect and addresses the above mentioned problems.

According to an aspect of the invention, there is provided a composition for use in treating a surface, comprising a polyorganosiloxane having the formula A and an active agent.

Formula A

T. R.sup.1 R.sup.2 SiO(R.sup.3 R.sup.4 SiO).sub.r (R.sup.5 T. SiO).sub.s SiR.sup.2 R.sup.1T

wherein

the symbols R.sup.1, R.sup.2, R. sup.3, R.sup.4 and R.sup.5, which are identical or different, represent a phenyl or a C.sub.1 to C.sub.6 alkyl radical,

the symbols T, which are identical or different, represent a phenyl, a C.sub.1 to C.sub.6 alkyl radical, or

a polyoxyalkylene ether residue of formula:

--R--O--(R'O).sub.n R"

or a amino group of formula:

$--(NR'R'')^{+}Z^{-}$

wherein R' and R'' are identical or different and represent a Csub1 to Csub19 alkyl radical or Csub3 to Csub15 alkylene group or branched Csub4 to 15 alkylene

group, the unit (R'O).sub.n represents a poly(ethylenoxy) or poly(propylenoxy) group, n is an average value ranging from 5 to 200, and Z represents an acetate anion.

r is an average value ranging from 1 to 10, and which interact with said biocidal agent.

s is an average value ranging from 1 to 100

According to a further aspect of the invention, there is provided a process for use in treating a surface, comprising applying an effective amount of a composition having a polyorganosiloxane of the formula A and an active agent to the surface.

According to another aspect of the invention, there is provided an article treated with a composition, the composition comprising a polyorganosiloxane having the formula A and an active agent.

The active agent of the composition of the invention may be selected from the group consisting of a biocidal, anti-microbial, bactericidal, fungicidal, germicidal, yeasticidal, moldicidal, algicidal and virucidal agent. The active agent or combination of agents selected may depend on the polymer composition used and on the intended use of the composition, in particular may be based on the type of micro organism that is required to be killed by treatment of the surface or implement with the composition of the invention.

It is preferred that the active agent comprises one or more biocidal agents.

The biocidal agent may be selected from cationic, amphoteric, amino, phenolic and halogen containing biocides. Examples of the biocides which may be used include:

Cationic biocides such as quaternary monoammonium salts, for example Cocoalkylbenzyldimethylammonium, $C_{12}-C_{14}$ alkylbenzyldimethylammonium, cocoalkyldichlorobenzyldimethylammonium, tetradecylbenzyldimethylammonium, didecyldimethylammonium and dioctyldimethylammonium chlorides,

Myristyltrimethylammonium and cetyltrimethylammonium bromides,

Monoquaternary heterocyclic amine salts such as laurylpyridinium, cetylpyridinium and $C_{12}-C_{14}$ alkylbenzyldimethylammonium chlorides,

Triphenylphosphonium fatty alkyl salts such as myristyltriphenylphosphonium bromide;

Polymeric biocides such as those derived from the reactions

Of epichlorohydrin and dimethylamine or diethylamine,

Of epichlorohydrin and imidazole,

Of 1, 3-dichloro-2-propanol and dimethylamine,

Of 1, 3-dichloro-2-propanol and 1, 3-bis (dimethylamino)-2-propanol,

Of ethylene dichloride and 1, 3-bis(dimethylamino)-2-propanol,

Of bis (2-chloroethyl) ether and of N, N'-bis (dimethylaminopropyl)urea or –thiourea,

Biguanidinc polymer hydrochlorides.

Amphoteric biocides such as derivatives of N-(N'- C_8 – C_{18} alkyl-3-aminopropyl)glycine, of N-(N'-(N''- C_8 – C_{18} alkyl-2-aminoethyl)-2-aminoethyl) glycine, of N,N-bis(N'- C_8 – C_{18} alkyl-2-aminoethyl)glycine, such as (dodecyle)

(aminopropyl) glycine and (dodecyl) (diethylenediamine) glycine;

Amines such as N-(3-aminopropyl)-N-dodecyl-1,3-propanediamine;

Phenolic biocides such as para-chloro-meta-xylenol, dichloro-meta-xylenol, phenol, cresols, resorcinol, resorcinol monoacetate, and their derivatives or water-soluble salts;

Halogenated biocides such as iodophores and hypochlorite salts, for example sodium dichloroisocyanurate;

5-chloro-2-methyl-4-isothiazolin-3-one; and

2-methyl-4-isothiazolin-3-one.

The active agent may preferably be contained in a non volatile carrier. The non-volatile carrier may be water, a glycol, an ester derivative of a glycol or an ether derivative of a glycol. In particular, alkylene glycols and poly alkylene glycols such as diethylene glycol and polyethylene glycol may be used. Alternatively, the carrier may be an alcohol having from 3 to 30 carbon atoms, preferably at least 10 carbon atoms.

Preferably, the polyorganosiloxane of the invention has the formula B:

Formula B

T (Me)sub2 SiO(SiMe.sub.2 O).sub.r (SiMeTO).sub.s SiMe.sub.2 T

wherein:

r is an average value ranging from 1 to 10, s is an average value ranging from 1 to 100,

T represents an amino group of formula:

--(NMe(CHsub2)sub11/13Me)$^{+}$ Z^{-}

wherein Z represents an acetate anion.

The polyorganosiloxane may be present in the composition in an amount of 10% to 50% by weight based on the weight of the composition. It is particularly preferred that the polyorganosiloxane is present in an amount of from 30% to 40% by weight based on the weight of the composition.

The active agent in the composition may be present in an amount of from 0.1% to 20% by weight based on the weight of the composition. It is particularly preferred that the active agent is present in an amount of from 0.5% to 11% by weight based on the weight of the composition.

The polyorganosiloxane and the active agent may represent the main ingredients of the composition of the invention. The composition may further comprise other ingredients, such as surfactants, chelating agents (such as aminocarboxylates, (ethylenediaminetetra-acetates, nitrilotriacetates, N,N-bis(carboxymethyl)-glutamates, citrates), alcohols (ethanol, isopropanol, glycols) detergency adjuvants (phosphates, silicates), dyes, and fragrances.

The surfactants which may be present in the composition of the invention may include: non-ionic surfactants such as ethylene oxide/propylene oxide block polymers, polyethoxylated sorbitan esters, fatty esters of sorbitan, ethoxylated fatty esters (containing from 1 to 25 units of ethylene oxide) polyethoxylated $C_8 - C_{22}$ alcohols (containing from 1 to 25 units of ethylene oxide), polyethoxylated $C_6 - C_{22}$ alkylphenols (containing from 5 to 25 units of ethylene oxide), alkylpolyglycosides,

amine oxides (such as C_{10} – C_{18} alkyldimethylamine oxides, C_8 – C_{22} alkoxyethyldihydroxyethylamine oxides) amphoteric or zwitterionic surfactants such as C_6 – C_{20} alkylamphoacetates or amphodiacetates (such as cocoamphoacetates), C_{10} – C_{18} alkyldimethylbetaines, C_{10} – C_{18} alkylamidopropyldimethylbetaines, C_{10} – C_{18} alkyldimethylsulphobetaines, C_{10} – C_{18} alkylamidopropyldimethylsulphobetaines.

The composition may preferably be in the form of an aqueous composition.

Advantageously, the polyorganosiloxane acts as a carrier to introduce the active agent to the surface, implement or the like to be treated by the composition of the invention. The amino and/or polyether functions on the polyorganosiloxane allow adhesion to the treated surface by preferentially interacting with the biocidal agents and the surface.

The composition of the invention provides disinfection of surfaces for a considerable time after application and will remain active after washing and/or abrading (polishing). This is advantageous over conventional biocides which quickly lose their efficacy after application particularly when the treated surface is washed or abraded.

The composition may be applied to a surface or implement, for example a floor, wall or medical instrument, in the form of a coating and the polymer assists in adhering the active agent to the surface or the implement. The biocides in the composition of the invention are held to the treated surface by a polymer which is based on a polyorganosiloxane. This prevents the biocides from leaving the surface during

washing or when abraded.

The composition of the invention may advantageously be incorporated into other materials. Such materials may include coatings such as paints and varnishes, which may be oil based or water soluble. The composition may also be incorporated into settable or curable compositions such as fillers, grouts, adhesives, mastics, putties and other materials which form a solid matrix over a period of time. Such prior art compositions are prone to the growth of mould and fungus, particularly in damp environments such as bathrooms and kitchens.

The composition of the invention may also be incorporated into plastics materials which may then be used to manufacture food processing implements, work surfaces, packaging materials, containers, and furniture for bathrooms, kitchens, hospitals and the like.

When the composition is applied to a surface or instrument, it may form a coating layer thereon which contains one or more active agents, preferably biocidal agents, so that any micro organisms present on or subsequently contacting the surface or instrument are killed. If the composition further comprises a surfactant, this may enhance the spreading ability of the composition over substantially the entire surface whilst imparting cleaning and detergent properties to the composition.

The composition is effective at killing micro organisms under dry or wet conditions.

The composition of the invention may be used to disinfect any suitable surface or implement, for example floors, walls, work surfaces, kitchen utensils, surgical instruments and the like. Advantageously, the composition may be used in different environments, that is in the medical or health care industry, for example in hospitals, in the food industry, for example in manufacturing plants and restaurants, in the commercial environment, for example in offices, and in the domestic environment, for example in kitchens and bathrooms.

The composition may be used to treat different surfaces, such as, for example, those made from ceramic, glass, pvc, formica or other polymeric materials, stainless steel, aluminium and wood.

The composition may be diluted before applying it to a surface or implement, such as by 1 to 100 fold or 1 to 1000 fold.

The composition may be effective at controlling the proliferation and/or elimination of many types of micro organisms, including gram-positive and gram-negative bacteria, such as: Bacillus cereus, Bacillus subtilis, Brevibacterium ammoniagenes, Brucella abortus, Klebsiella pneumonia, Lactobacillus casei, Proteus vulgaris, Listeria monocytogenes, Pseudomonas aeruginosa, Salmonella gallinarum, Salmonella typhosa, Staphylococcus aureus, Steptococcus faecalis, Flavobacterium species, Bacillus species, Escherichia species, Aeromonas species, Anchromobacter species and Alcaligenes species, fungi such as: Cephalosporium species, Cladosporium species, Fusarium species, Paecilomyces species, Penicillium species, Streptomyces

species, Trichophyton interdigitale, Chaetorarium globesom, Aspergillus niger, and Ceniphora puteana, Cornyebacterium species, Proteus penneri, Enterobacter aerogenes, Salmonella enteritidis; yeasts such as Monilia albicans and Saccharomyces cerevisiae, Candida albicans; algae such as Chlorella pyrenoidosa Chlorella vulgaris, Nostoc commune, Scenedesmus vacuolatus ; and Anabaena cylindrical; and moulds such as Epidermophyton floccosum, Microsporum canis, Tricophyton mentagrophytes and Candida albicans.

Embodiments of the present invention will now be described by way of non-limiting example only:

A. Biocidal activity of this solution was tested according to the standard suspension test prEN 13713 under the following conditions

Diluent	water
Test strain	Pseudomonas aeruginosa
	Staphylococcus aureus
	Enterococcus hirae
	Escherichia coli
Temperature	20 degree C
Contact time	5 minutes
Interfering substance	Dehydrated yeast and bovine serum albumin (10%)
Neutralizing agent	Lecithin 0.3%, polysorbate 80 (3%), sodium thiosulphate

(0.5%), L-histidine (0.1%) saponine (3%) in diluent

Results

Log 5 reduction in all bacteria at dilution of 1 in 20.

B. Demonstration of the residuality of the biocide.

The formulation was prepared by measuring the required volume of the biocides with a pipette and adding them to a 100ml volumetric flask. The volume of polymer required was also measured and added.

The formulation was prepared according to the following recipe:

Raw Material 1	8.0 %	(1.5 % active 3:1 CIT:MIT)
Raw Material 2	20 %	(50 % active Quaternary alkylbenzyl dimethylammonium chloride)
Raw Material 3	30 %	(Approx. 20 % active polymer)
Water	42 %	

[CIT – choromethylisothiazolone, MIT – methylisothiazolone]

The solution was mixed on a shaker and the volume adjusted to 100ml with water. Three dilutions of the formulation were tested, concentrated, 1 in 10 and 1in 20. The diluent used was water.

1. Using each of the dilutions (concentrated, 1 in 10 and 1 in 20), the inside of three small petri dishes (total of 9 petri dishes) were coated and left to dry.

2. At the same time, innoculate bacterial culture from frozen stock were placed into universals containing 10ml Mueller Hinton Broth and incubated for 24 hours at 37 Deg C in a shaking incubator set at 100rpm.

3. The culture was diluted in PBS such that there are 10^8 bacteria ml^{-1}. 550µl is added to each plate and 100µl immediately removed for sampling.

4. The plates were incubated at room temperature.

5. A further 100ml was removed for sampling at 1 and 5 minutes and 3 x 20µl removed for plating of neat solution where required.

6. Steps 3 and 4 were repeated at 72 hours and 7 days.

Sampling

1. 100µl of sampled culture was added to 900µl of sterile PBS pre-prepared eppindorfs.

2. Serial dilutions were made in PBS

3. 3x20µl of each dilution was added to nutrient agar plates

4. Drops were allowed to dry and then the plates incubated for 24 hours for *S. enteritidis, E. coli 0157.*

Results

The number of CFU (colony forming units) formed in each 20µl drop was counted and the average of three calculated. This was multiplied by the dilution factor to give the number of cfu per millilites of culture (cfu ml-1)

Escherichia coli 0157			
	1 day	2 day	7 day
Blank			
T=1min	4.5×10^8	4.1×10^8	9.1×10^7
T=5min	5.5×10^8	4.1×10^8	9.0×10^7
Biocides only			
T=1min	BLD	BLD	3.2×10^4
T=5min	BLD	BLD	BLD
Concentrated formulation			
T=1min	BLD	BLD	BLD
T=5min	BLD	BLD	BLD
Diluted formulation 1in10			
T=1min	BLD	BLD	BLD
T=5min	BLD	BLD	BLD
Diluted formulation 1in20			
T=1min	BLD	BLD	BLD
T=5min	BLD	BLD	BLD
BLD= <50 cfu ml^{-1}			

Salmonella enteritidis			
	1 day	2 day	7 day
Blank			
T=1min	1.31×10^8	9.75×10^7	1.21×10^7
T=5min	1.36×10^8	1.38×10^8	1.43×10^7
Biocides only			
T=1min	BLD	BLD	1.2×10^7
T=5min	BLD	BLD	BLD
Concentrated formulation			
T=1min	BLD	BLD	BLD
T=5min	BLD	BLD	BLD
Diluted formulation 1in10			
T=1min	BLD	BLD	BLD

T=5min	BLD	BLD	BLD
Diluted formulation 1in20			
T=1min	BLD	BLD	BLD
T=5min	BLD	BLD	BLD

BLD= <50 cfu ml^{-1}

C. Durability of residual biocide to washing and wiping

The following experiment was carried out to test the resistance of the biocide to being washed or wiped after drying and to compare this to biocides alone.

Method

1. Formulation was prepared as above and diluted to a 1 in 10 dilution with water (Solution 1) A second solution was prepared using the same quantities of biocides as in A but without the polymer (Solution 2).

2. 9 glass beakers were sprayed with Solution 1, 2 or water (3 beakers of each).

3. The beakers were either left to dry (7 hours), left to dry then rinsed with 25ml of water, or left to dry and wiped with a soft cloth (see Table of treatments shown below)

Treatment		
Left to dry (7 hours)	Solution 1	Solution 2
Left to dry and rinsed with 25 ml water	Solution 1	Solution 2
Left to dry and wiped soft cloth	Solution 1	Solution 2
Left to dry	Water	Water

24 hours later 10^8 cfu of E. coli 0157 are pipetted onto the surface of the beakers and 100µl aliquots removed at 0, and 15 minutes. The number of viable bacteria will be counted and reported as cfu ml^{-1}.

Results

	Solution 1		Solution 2	
Treatment	0 min	15 min	0 min	15 min
Left to dry (7 hours)	$1x10^2$	BLD	$2.1x10^3$	BLD
Left to dry and rinsed with 25 ml water	$7x10^8$	$8x10^2$	$1x10^9$	$1x10^9$
Left to dry and wiped soft cloth	$4x10^8$	BLD	$5x10^2$	BLD

Treatment	0 min	15 min
Control (sprayed with water and left to dry)	$> 1x\ 10^9$	$> 1x\ 10^9$

BLD < 100 cfu

Accordingly, solution 1 demonstrates a greater durability to washing and wiping then solution 2.

D. Further Comparative Formulations

The following formulations were prepared. The difference between the formulations residing in the type and quantity of isothiazolone content:

Components.	CAS No.
5-Chloro-2-methyl-2H-isothiazol-3-one	26172-55-4
2-Methyl-2H-isothiazol-3-one	2682-20-4
1,2-benzisothiazol-3(2H)-one	2634-33-5
Cocoalkyldimethylbenzylammonium chloride	61789-71-7
Di-n-decyl dimethylammonium chloride	7173-51-5
Propan-2-ol	67-63-0
Di-quaternary terminated polydimethylsiloxane	Polymer
Aliphatic alcohol ethoxylate	
Water	

Formulations	A	B	C
Raw Material 1	8.0%	Zero	Zero
Raw Material 2	Zero	8.0%	Zero
Raw Material 3	5.0%	5.0%	6.0%
Raw Material 4	11.0%	11.0%	12.0%
Raw Material 5	30.0%	30.0%	30.0%
Water	46.0%	46.0%	52.0%

Raw Material 1 is a mixture of benzisothiazolone and methylisothiazolone at 5% total activity.

CAS Nos. 2634-33-5 and 2682-20-4

Raw Material 2 is a mixture of chloromethylisothiazolone and methylisothiazolone at

1.5% total activity.

CAS Nos. 26172-55-4 and 2682-20-4

Raw Material 3 is a solution of cocoalkyl dimethylbenzyl ammonium chloride at 50% activity.

CAS No. 61789-71-7

Raw Material 4 is a solution of 50% di-n-decyl dimethyl ammonium chloride stablised with 20% propan-2-ol.

CAS Nos. 7173-51-5 and 67-63-0

Raw Material 5 is an appoximate 20 % solution of a di-quaternary terminated polydimethylsiloxane polymer stabilised with an alophatic alcohol ethoxylate at <5% (CAS Nos. not available).

E. Shelf-Life

The isothiazolone type and content of each formulation influences in particular, the shelf life of the formulation. For example, the shelf life of formulation C is greater than that of formulation B, which in turn is greater than that of formulation B, as exemplified below:

Accelerated ageing tests carried out over 48 hours:

Formulation C has an indefinite shelf life, as shown from accelerated ageing tests at up to 60 °C for 48 hours, where no visible changes were observed.

Formulation B has a shelf-life of at least 3 months. However, a colour change is observed after 40 hours during accelerated ageing tests carried out at 60 °C. The concentration of CIT in the formulation dropped to about 60 % of its original value after 3 months natural storage, whilst the MIT concentration remained at over 90 %.

Formulation A demonstrated a shelf-life of at least six months in corresponding accelerated ageing tests.

Accelerated aging tests carried out over 65 hours:

At 60 °C for 65 hours, formulation C remained unchanged, whilst formulation A demonstrated only marginal changes. The observed changes affected only the isothiazolones in the formulation and do not compromise the remainder of the formulation.

F. Kill Rates

The kill rate per minute was measured for each formulation against *E.coli* (0157), *S.enteritidis*, *K.pneumoniae*, *C.albicans* and MRSA by applying a 7 day application of a 1:20 dilution. This 7 day application of a 1:20 dilution involves challenging treated surfaces with bacteria after increasing lengths of time to see if the bactericide was still working, as follows:

A batch of clean plates were sprayed with the appropriately diluted formulation and leaving to dry. After various time intervals, the plates were then challenged with

bacterial cultures and incubated for testing. The resulting plates were then compared with plates sprayed with the same bactericide in the absence of polymer.

Result

A 100 % kill rate in 1 minute was achieved against all the above-mentioned bacteria by a 1:20 dilution of the formulation.

The speed of kill for each formulation appears to corresponds to the stability of the formulation in that the lower the stability of the formulation, the greater the speed of kill, such that formulation B demonstrates a greater speed of kill that formulation A, which in turn demonstrates a greater speed of kill than formulation C. However, for the application to which a residual biocide may be put, speed of kill is less important since, by definition, residual biocides have long contact times. Hence, under the expected conditions of use, all three formulations performed to a similar level.

The formulations exemplified above exhibit antibacterial activity, as evidenced by the biocidal properties of the formulations. The kill spectrum is very similar for all of formulations A, B and C. In addition, these particular formulations also have proven fungicidal properties.

This ability to effectively disinfect surfaces of bacteria, fungi (including yeast) as well as remain useable over a significant period of time allows the use of the formulations as disinfecting agents for the treatment of surfaces in, for example, the food and beverage industry, hospitals and the veterinary industry, where the formulations may

be used, for example, to treat working surfaces and equipment, all industries in which high regulatory standards are applied and strict controls are maintained in respect of hygiene.

Efficacy against Mycobacterium

The formulations A, B and C demonstrate a low speed of kill for Mycobacterium. In order to guarantee an efficient kill speed, the pH needs to be carefully controlled. As an example, formulation D (detailed below) demonstrates excellent results against Mycobacterium.

Formulation D:

Raw Material 4	14.0 %
Raw Material 5	30.0 %
Raw Material 6	8.0 %
Raw Material 7	8.0 %
Raw Material 8	5.0 %
Water	35.0 %

Raw Materials 4&5 are as for formulations A, B and C

Raw material 6 is 2-aminoethanol, CAS No. 141-43-5.

Raw Material 7 is a 30% solution of trisodium ethylenediamine disuccinate, CAS No. 178949-82-1.

Raw Material 8 is a 90% solution of an alcohol ethoxylate, CAS No. 68439-45-2.

[N.B. Raw Material 7 can be replaced by 6% of Raw Material 9, a 40% solution of tetrasodium ethylenediamine tetra-acetate, CAS No. 64-02-8, increasing the water to 37.0% to make Formulation E.]

The proved efficacy of formulations D and E against Mycobacterium makes the formulations of exceptional value in medical applications and food preparation environments where regulatory standards relating to the specified efficacies of utilised formulations are high and stringent controls are in place to ensure that the standards are being met by any formulation approved for such application.

CLAIMS

1. A composition for use in treating a surface, comprising a polyorganosiloxane having the formula A

Formula A

T. R.sup.1 R.sup.2 SiO(R.sup.3 R.sup.4 SiO).sub.r (R.sup.5 T. SiO).sub.s SiR.sup.2 R.sup.1T

wherein

the symbols R.sup.1, R.sup.2, R. sup.3, R.sup.4 and R.sup.5, which are identical or different, represent a phenyl or a C.sub.1 to C.sub.6 alkyl radical,

the symbols T, which are identical or different, represent a phenyl, a C.sub.1 to C.sub.6 alkyl radical, or

a polyoxyalkylene ether residue of formula:

--R--O--(R'O).sub.n R"

or a amino group of formula:

$--(NR'R'R'')^{+} Z^{-}$

wherein R' and R'' are identical or different and represent a Csub1 to Csub19 alkyl radical or Csub3 to Csub15 alkylene group or branched Csub4 to 15 alkylene group, the unit (R'O).sub.n represents a poly(ethylenoxy) or poly(propylenoxy) group, n is an average value ranging from 5 to 200, and Z represents an acetate anion.

r is an average value ranging from 1 to 10, and which interact with said biocidal agent.

s is an average value ranging from 1 to 100;

and an active agent.

2. A composition according to Claim 1 wherein the polyorganosiloxane has the formula B:

T (Me)sub2 SiO(SiMe.sub.2 O).sub.r (SiMeTO).sub.s SiMe.sub.2 T

wherein:

r is an average value ranging from 1 to 10, s is an average value ranging from 1 to 100,

T represents an amino group of formula:

--(NMe(CHsub2)sub11/13Me)$^{+}$ Z^{-}

wherein Z represents an acetate anion.

3. A composition according to Claim 1 or Claim 2, in which the active agent is selected from the group consisting of a biocidal, anti-microbial, bactericidal, fungicidal, germicidal, yeasticidal, moldicidal, algicidal and virucidal agent.

4. A composition according to any one of Claims 1 to 3, in which the active agent comprises one or more biocidal agents.

5. A composition according to any preceding claim, in which the polyorganosiloxane is present in an amount of 10 % to 50 % by weight based on the

weight of the composition.

6. A composition according to any preceding claim, in which the active agent is present in an amount of 0.1% to 20% by weight based on the weight of the composition.

7. A composition according to any preceding claim, further comprising a surfactant.

8. A composition according to any preceding claim, in which the active agent is contained in a non-volatile carrier.

9. A composition according to any preceding claim, which is in the form of an aqueous composition.

10. A composition according to any preceding claim, which is incorporated into a functional material or article.

11. A composition according to Claim 10, in which the functional material is a coating material, a cleaning material or a building material.

12. A process for use in treating a surface, comprising applying an effective amount of a composition having a polyorganosiloxane of the formula A:

Formula A

T. R.sup.1 R.sup.2 SiO(R.sup.3 R.sup.4 SiO).sub.r (R.sup.5 T. SiO).sub.s SiR.sup.2 R.sup.1T

wherein

the symbols R.sup.1, R.sup.2, R. sup.3, R.sup.4 and R.sup.5, which are identical or different, represent a phenyl or a C.sub.1 to C.sub.6 alkyl radical,

the symbols T, which are identical or different, represent a phenyl, a C.sub.1 to C.sub.6 alkyl radical, or

a polyoxyalkylene ether residue of formula:

--R--O--(R'O).sub.n R"

or a amino group of formula:

$--(NR'R'')^{+}Z^{-}$

wherein R' and R'' are identical or different and represent a Csub1 to Csub19 alkyl radical or Csub3 to Csub15 alkylene group or branched Csub4 to 15 alkylene group, the unit (R'O).sub.n represents a poly(ethylenoxy) or poly(propylenoxy) group, n is an average value ranging from 5 to 200, and Z represents an acetate anion.

r is an average value ranging from 1 to 10, and which interact with said biocidal agent.

s is an average value ranging from 1 to 100;

and an active agent to the surface.

13. A process according to Claim 12 wherein the polyorganosiloxane has the Formula B:

T (Me)sub2 SiO(SiMe.sub.2 O).sub.r (SiMeTO).sub.s SiMe.sub.2 T

wherein:

r is an average value ranging from 1 to 10, s is an average value ranging from 1 to 100,

T represents an amino group of formula:

--(NMe(CHsub2)sub11/13Me)$^{+}$ Z^{-}

wherein Z represents an acetate anion.

14. An article which has been treated by the composition according to any of Claims 1 to 9.

INTERNATIONAL SEARCH REPORT

ational Application No
/GB2004/003121

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A01N25/10 A01N25/30 A01N33/12 A01N43/80
//(A01N33/12,25:30,25:10),(A01N43/80,25:30,25:10)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00/00024 A (DOROTHY JOHN ; RAWDON DAVID (GB); WOOLLARD TREVOR (GB)) 6 January 2000 (2000-01-06) page 1, paragraphs 1,4 page 2, paragraph 1-4 page 3, paragraph 4 - page 4, paragraph 2 page 4, paragraph 5 - page 5, paragraph 1 page 5, paragraphs 5,6 page 6, paragraph 7 - page 7, paragraph 4 page 7, paragraph 7 page 8, paragraph 2 pages 9-10 & GB 2 338 651 A (WOOLLARD TREVOR P ; DOROTHY JOHN (GB); RAWDON DAVID (GB)) 29 December 1999 (1999-12-29) cited in the application ----- -/—	1,3,4, 6-12,14

[X] Further documents are listed in the continuation of box C. [X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
6 October 2004	21/10/2004

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Marie, G

Form PCT/ISA/210 (second sheet) (January 2004)

INTERNATIONAL SEARCH REPORT

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 737 420 A (OSI SPECIALTIES INC) 16 October 1996 (1996-10-16) page 2, lines 41-57 example 1 claims 1,4,5,9,11,16	1,3-5, 7-9,14
X	WO 96/19194 A (HUGHES IAIN ALLAN ; PROCTER & GAMBLE (US)) 27 June 1996 (1996-06-27) page 1, paragraph 2 page 4, paragraph 1 page 4, paragraph 6 - page 5, last line page 6, paragraph 3 page 7, paragraph 2 page 8, paragraph 4 claims 1,2,4,7	1,3-5, 7-12,14
X	WO 86/03374 A (ADAMS VETERINARY RES LAB) 19 June 1986 (1986-06-19) page 9, paragraph 2 page 12, line 15 - page 16, line 18 examples III,VII,XI,XVI,XIX claims 1-4	1,3,4,6, 9,12,14
X	DATABASE WPI Section Ch, Week 199522 Derwent Publications Ltd., London, GB; Class C01, AN 1995-167152 XP002299377 & JP 07 089817 A (NIPPON SODA CO) 4 April 1995 (1995-04-04) abstract	1,3,4, 6-9,12, 14

1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB2004/003121

Box II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

In formula A, the symbol T can represent a polyoxyalkylene ether residue of formula -R-O-(R'O)n-R''. Insofar as subsitutents R and R'' are neither defined in the claims nor in the description, no meaningful search can be carried out (Articles 5 and 6 PCT).
The search has therefore been restricted to compositions, processes and articles comprising a polyorganosiloxane having the formula A wherein T represents a phenyl, C1-C6 alkyl radical or an amino group as defined in page 23, line 19-24.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.5), should the problems which led to the Article 17(2) declaration be overcome.

INTERNATIONAL SEARCH REPORT

International Application No
/GB2004/003121

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